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Title: Innovative MXene substrates as Surface Enhanced Raman Scattering active platforms

Abstrakt: Surface Enhanced Raman Spectroscopy (SERS) is an ultrasensitive method that enables simple and reliable identification of small quantities of molecules. SERS analysis is non-destructive, fast, with high accuracy, and is widely explored for chemical and biological sensing and detection. The signal enhancement is attributed to the electromagnetic and chemical mechanisms. The electromagnetic mechanism relies on the generation of localized surface plasmons leading to a significant enhancement of the incident electromagnetic field at hot spots of the plasmonic materials which are typically noble and coinage metals with nanoscale surface roughness. The chemical mechanism is related to the interaction between the analyte molecules and the SERS substrate surface such as charge transfer processes, resonant energy transfer, or modification of the electronic structure of the analyte molecule. At present the research is focused on new noble metal-free SERS substrates based predominantly on low-dimensional semiconducting nanomaterials (nanoparticles, nanosheets). Here the signal enhancement is mainly attributed to the photoinduced charge transfer of the chemical mechanism. The basic aim of this thesis is the research and development of the Ti3C2Tx MXene nanoflakes-based SERS substrates and studies of the effect of the active layer morphology on the SERS effect. Few-layer Ti3C2Tx MXene substrates fabricated by vacuum-assisted filtration (VAF) and spray coating on filter paper and glass were prepared and studied. The VAF deposition results in a dense and compact MXene layer suitable for SERS with high spot-to-spot and substrate-to-substrate reproducibility with a significant limit of detection (LoD) of 20 nM for Rhodamine B analyte. The spray-coated MXenes film on paper revealed lower uniformity, with a LoD of 50 nM for the drop-casted analyte. The prepared MXenes films were analyzed by AFM, SEM, confocal laser scanning micrsopy and confocal Raman microscopy. For MXene layers prepared by spray-coating we observed formation of aggregates during the deposition process for both glass and paper substrates. This effect was not observed for VAF deposited MXene films. Accumulation of the analyte molecules in the vicinity of MXene aggregates negatively affects the resulting SERS enhancement. Ti3C2Tx MXene layers deposited on filter paper by VAF offer great potential as a cost-effective, easy-to-manufacture, yet robust platform for sensing applications. It is demonstrated that the deposition by vacuum-assisted filtration (VAF) method enables the preparation of dense MXene layers suitable for SERS with high uniformity simply without any complicated deposition equipment. The results point to the dominant role of the

chemical mechanism for SERS which is assumed for noble metal-free SERS substrates.

Povrchovo zosilnená Ramanova spektroskopia (SERS) je vysoko citlivá metóda, ktorá umožňuje jednoduchú a spoľahlivú identifikáciu malého počtu molekúl skúmanej látky. Analýza SERS je nedeštruktívna, rýchla, s vysokou presnosťou a je široko využívaná pre chemické a biologické snímanie a detekciu. Zosilnenie signálu sa pripisuje elektromagnetickému a chemickému mechanizmu. Elektromagnetický mechanizmus vychádza z generovania lokalizovaných povrchových plazmónov, čo vedie k významnému zosilneniu dopadajúceho elektromagnetického poľa na „horúce“ miesta plazmonických materiálov. Sú to typicky vrstvy ušľachtilých kovov s drsnosťou povrchu na nanoúrovni. Chemický mechanizmus súvisí s interakciou medzi molekulami analyzovanej látky a povrchom SERS substrátu, ako sú procesy prenosu náboja, rezonančný transfer energie alebo modifikácia elektronickej štruktúr. V súčasnosti sa výskum zameriava na nové nekovové substráty SERS založené prevažne na nízkorozmerných polovodičových nanomateriáloch (nanočastice, nanovločky). Tu sa zosilnenie signálu pripisuje hlavne fotoindukovanému prenosu náboja v rámci chemického mechanizmu. Hlavným cieľom dizertačnej práce je výskum a vývoj SERS substrátov na báze inovatívnych nanvločiek Ti3C2Tx MXénov a štúdium vplyvu morfológie aktívnej vrstvy na efekt SERS. Pripravili a skúmali sme SERS substráty na báze niekoľkovrstvových Ti3C2Tx MXénov, ktoré boli vyrobené vákuom asistovanou filtráciou (VAF) a striekaním na filtračný papier a na sklo. Výsledkom depozície VAF je kompaktná vrstva MXénov vhodná pre SERS, ktorá vykazuje vysokú reprodukovateľnosť vlastností v rámci substrátu ako aj pripravených substrátov s limitou detekcie (LoD) 20 nM pre analyzovanú látku rodamínu B. Striekaním deponovaná vrstva MXénov na papier ukázala nižšiu homogenitu a LoD 50 nM pre nakvapkaný rodamínB. Vrstvy MXénov pripravené VAF boli analyzované AFM a SEM, konfokálnou laserovou rastrovacou mikroskopiou a konfokálnou Ramanovou mikroskopiou. VAF vrstvy mali odlišnú morfológiu povrchu oproti striekaným vrstvám, na ktorých sme pozorovali formovanie agregátov, čo ovplyvnilo aj distribúciu analyzovanej látky na povrchu SERS vrstvy. Zvýšená akumulácia molekúl analyzovanej látky v blízkosti agregátov MXénov sa pozorovala predovšetkým pri depozícii kvapkaním čo následne negatívne ovplvnilo výsledné hodnoty SERS. Vrstvy Ti3C2Tx MXénov nanesené na filtračný papier metódou VAF ponúkajú veľký potenciál ako nízko-nákladová efektívna, ľahko vyrobiteľná, ale robustná platforma pre SERS aplikácie. Ukázali sme, že metóda nanášania vákuovou filtráciou umožňuje pripraviť kompaktnú vrstvu MXénov vhodnú pre SERS s vysokou rovnomernosťou jednoduchým spôsobom bez zložitého depozičného zariadenia. Výsledky sú v súlade s publikovanými dátami o dominantnej úlohe chemického mechanizmu pre SERS.

Surface Enhanced Raman Spectroscopy (SERS) is an ultrasensitive method that enables simple and reliable identification of small quantities of molecules. SERS analysis is non-destructive, fast, with high accuracy, and is widely explored for chemical and biological sensing and detection. The signal enhancement is attributed to the electromagnetic and chemical mechanisms. The electromagnetic mechanism relies on the generation of localized surface

plasmons leading to a significant enhancement of the incident electromagnetic field at hot spots of the plasmonic materials which are typically noble and coinage metals with nanoscale surface roughness. The chemical mechanism is related to the interaction between the analyte molecules and the SERS substrate surface such as charge transfer processes, resonant energy transfer, or modification of the electronic structure of the analyte molecule. At present the research is focused on new noble metal-free SERS substrates based predominantly on low-dimensional semiconducting nanomaterials (nanoparticles, nanosheets). Here the signal enhancement is mainly attributed to the photoinduced charge transfer of the chemical mechanism. The basic aim of this thesis is the research and development of the Ti3C2Tx MXene nanoflakes-based SERS substrates and studies of the effect of the active layer morphology on the SERS effect. Few-layer Ti3C2Tx MXene substrates fabricated by vacuum-assisted filtration (VAF) and spray coating on filter paper and glass were prepared and studied. The VAF deposition results in a dense and compact MXene layer suitable for SERS with high spot-to-spot and substrate-to-substrate reproducibility with a significant limit of detection (LoD) of 20 nM for Rhodamine B analyte. The spray-coated MXenes film on paper revealed lower uniformity, with a LoD of 50 nM for the drop-casted analyte. The prepared MXenes films were analyzed by AFM, SEM, confocal laser scanning micrsopy and confocal Raman microscopy. For MXene layers prepared by spray-coating we observed formation of aggregates during the deposition process for both glass and paper substrates. This effect was not observed for VAF deposited MXene films. Accumulation of the analyte molecules in the vicinity of MXene aggregates negatively affects the resulting SERS enhancement. Ti3C2Tx MXene layers deposited on filter paper by VAF offer great potential as a cost-effective, easy-to-manufacture, yet robust platform for sensing applications. It is demonstrated that the deposition by vacuum-assisted filtration (VAF) method enables the preparation of dense MXene layers suitable for SERS with high uniformity simply without any complicated deposition equipment. The results point to the dominant role of the chemical mechanism for SERS which is assumed for noble metal-free SERS substrates.

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